Coumarin-derivative-based off-on catalytic chemodosimeter for Cu^{2+} ions

Mi Hee Kim, Hyun Hye Jang, Sujung Yi, Suk-Kyu Chang and Min Su Han*

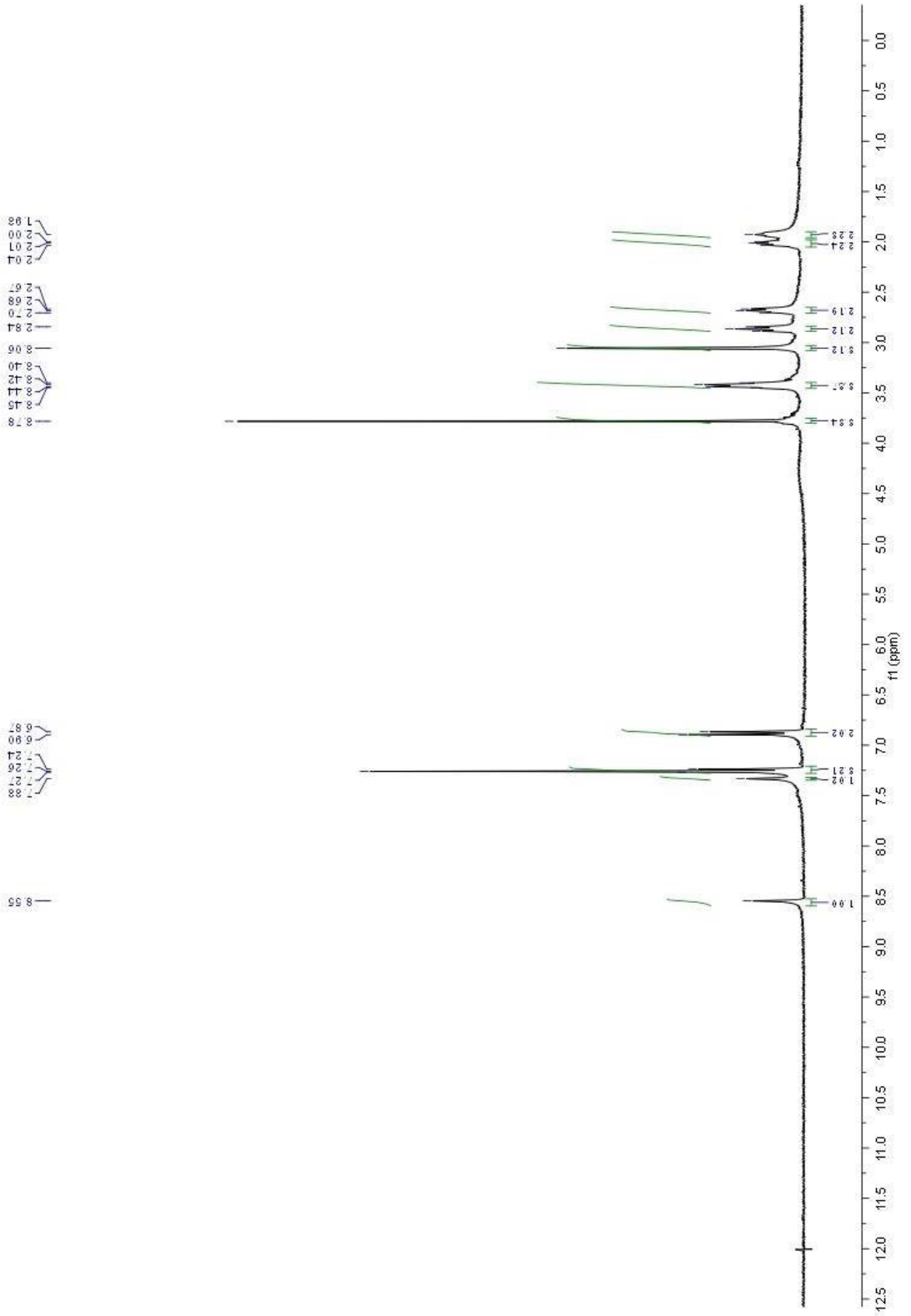
Synthesis of 1

To a coumarin 334 (100 mg, 0.35 mmol) in ethanol (3.0 mL) was added 4-methoxyphenylhydrazine (310 mg, 0.18 mmol). The reaction solution was stirred at room temperature for 12 hr. After filtration, the solid was washed with pure Ethanol and water. The product was obtained as a red solid in 54.6% yield. m.p. : 153.0 ~ 155.4℃
HPMS-DIP-Mass ; m/z Calcd for $C_{24}H_{25}N_3O_3$: 403.1896. Found, 403.1933

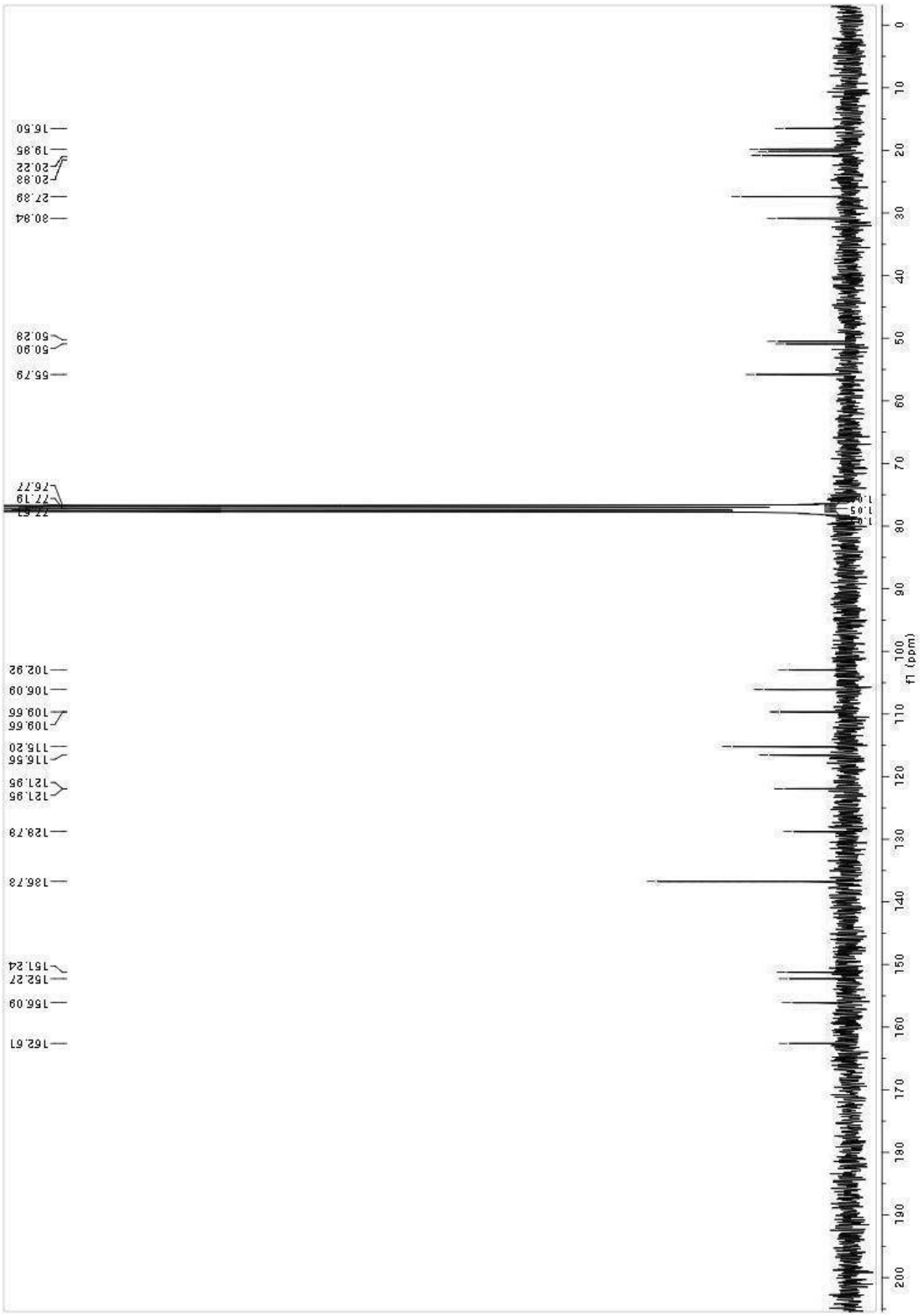
^{1}H NMR : 8.55(s, 1H), 7.33(s, 1H), 7.25(d, *J* = 9.0 Hz, 2H), 6.88(d, *J* = 9.0 Hz, 2H), 3.78(s, 3H), 3.43(m, 4H), 3.06(s, 3H) , 2.84(t, 2H), 2.68(t, 2H), 2.00(m, 4H)

^{13}C NMR : 162.61, 156.09, 152.27, 151.24, 136.73, 128.78, 121.95, 116.56, 115.20, 109.66, 106.09, 102.92, 55.79, 50.90, 50.29, 30.84, 27.39, 20.83, 20.22, 19.85.

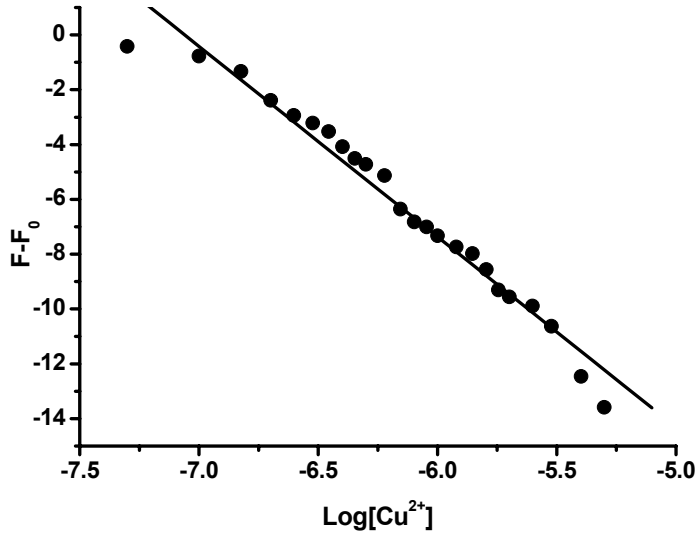
* ^{1}H-NMR (300MHz, $CDCl_3$) of **1**



* ^{13}C-NMR (75MHz, $CDCl_3$) of **1**



Determination of the detection limit of 1 for Cu^{2+}



The detection limit of **1** for Cu^{2+} was estimated from plot of normalized fluorescence changes of **1** verse Log[Cu^{2+}] using a equation (1).[1]

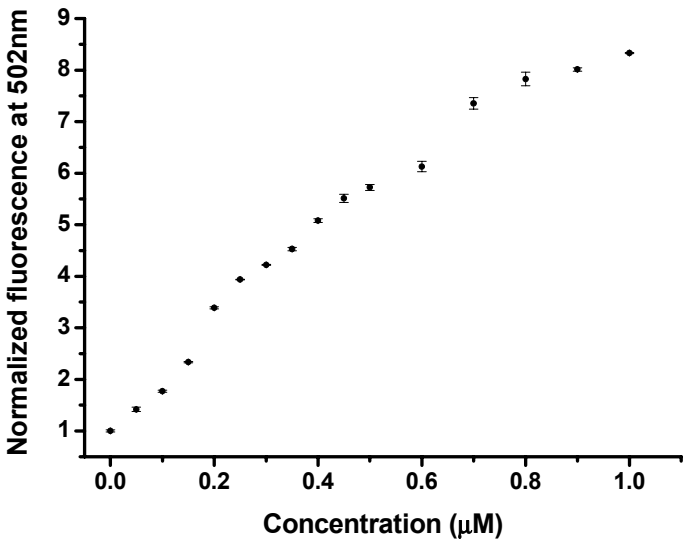
$$10^{-\left[\frac{\text{Slope}}{\text{Intercept}}\right]} \qquad \text{Equation 1}$$

Reference

1. M. Shortreed, R. Kopelman, M. Kuhn, B. Hoyland *Anal. Chem*. **1996,** *68*, 1414-1418.

Quantification of Cu^{2+}

The fluorescence intensities of the solutions were recorded 5 min after adding various concentrations of Cu^{2+} to the solutions of chemodosimeter (1 μM) in pH 5 buffer respectively



[Ligand] : 1μM

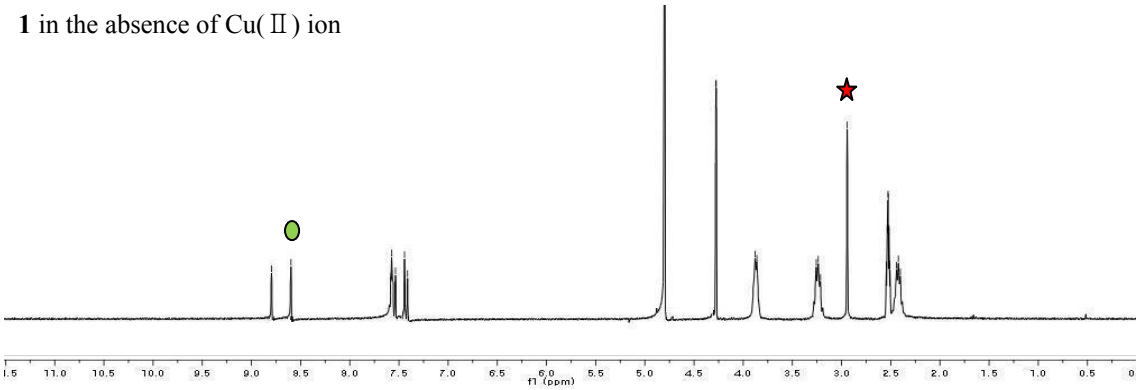
[Cu^{2+} ion] : from 0 to 1 μM

Buffer : Acetate buffer (pH 5.0)

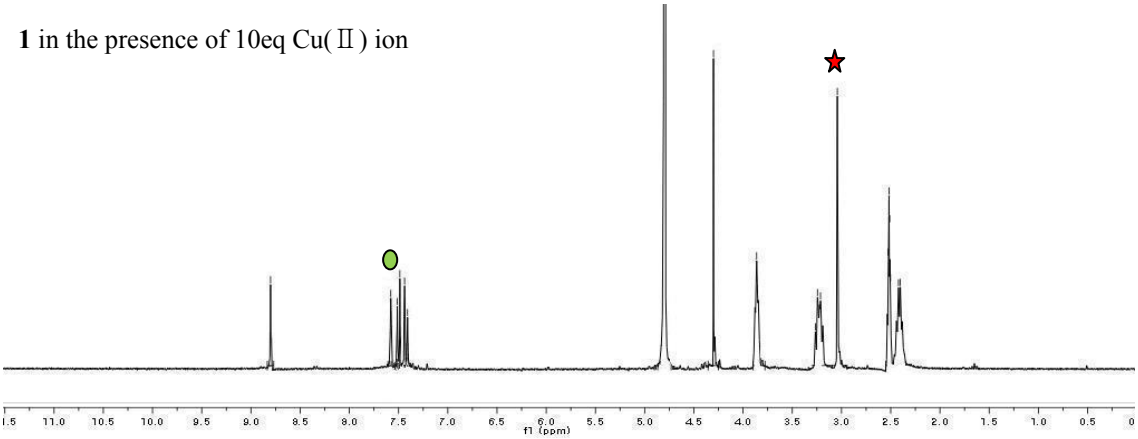
50% Acetonitrile

^{1}H-NMR spectra of 1, 1 + 10 eq Cu(II), and the mixture of coumarin 334 and 4-methoxyphenyl hadrazine

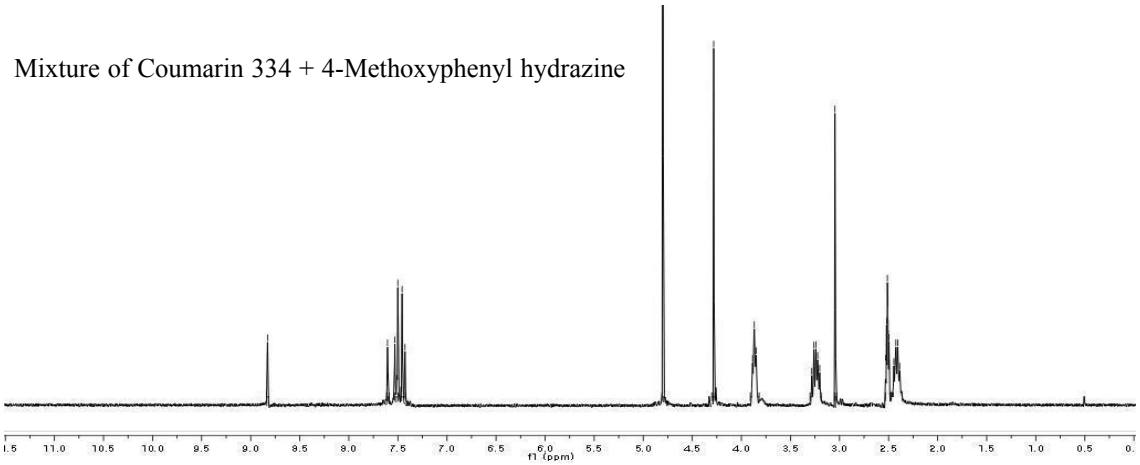
1 in the absence of Cu(Ⅱ) ion



1 in the presence of 10eq Cu(Ⅱ) ion

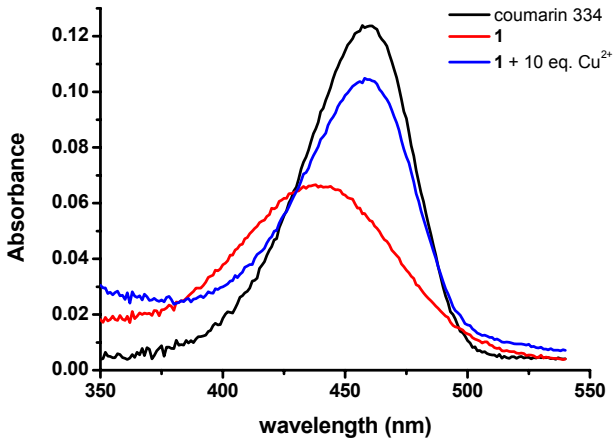


Mixture of Coumarin 334 + 4-Methoxyphenyl hydrazine



UV spectra & Fluorescence spectra of Coumarin 334 and 1+ 10eq Cu^{2+} ion

(1) UV spectra



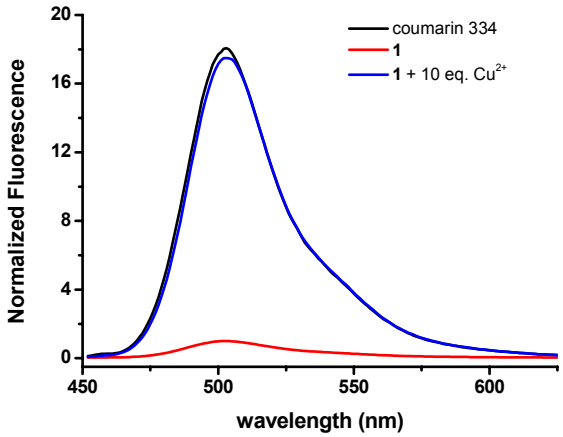
[Ligand] : 5μM

[Cu(II) ion] : 50μM

Buffer : Acetate buffer (pH 5.0)

50% Acetonitrile

(2) Fluorescence spectra



[Ligand] : 1μM

[Cu(II) ion] : 10μM

Buffer : Acetate buffer (pH 5.0)

50% Acetonitrile

λ_{ex} : 450nm